Effect of crystal lattice structure on the kinetics of hopping quenching of luminescence

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(Submitted 6 July 1983)
Zh. Eksp. Teor. Fiz. **86**, 1360–1364 (April 1984)

Asymptotic expressions are obtained, within the framework of the concepts of a regular equivalent donor lattice, for the kinetics of hopping quenching, with account taken of the nonzero donor–acceptor distance. The results of a numerical calculation of the time evolution of the donor excited state with and without allowance for the structure of the material are compared at various values of the parameters of the theory.

The hopping mechanism of energy transfer in an assembly of interacting donors and acceptors was proposed as an alternative to the diffusion mechanism in Refs. 1 and 2, where the concept of a regular equivalent donor lattice was used and the variation of the random instantaneous excitation-quenching rate was regarded as a Markov process. In later studies,[3–6] in particular, account was taken of a "memory" effect, i.e., of the possibility that an excitation can land repeatedly on one and the same site in the course of its wandering. The nonexponential kinetics of excitation outflow, due to the disorder of the donors, was also considered. The theoretical studies are of practical value, in particular, because they can be used to deduce the interaction mechanism from the experimental data and to determine the microparameters of the donor-donor (C_{DD}) and donor acceptor (C_{DA}) interactions. These are needed to calculate important material characteristics such as the luminescence quantum yield, the optimal active-impurity density, and others.

The microparameter C_{DD}, which characterizes the rate of donor–donor transfer, is usually determined from the section of the curve of stationary migrational quenching realized at long times, using asymptotic formulas that are valid at $t\to\infty$. This means, however, loss of the information contained on C_{DD} in the entire curve of the decay of the donor δ-excited state. In our opinion, the most consistent approach to the determination of C_{DD} is to describe the experimental curve, within the framework of the corresponding theory, in the entire time scale and to determine C_{DD} from the best agreement between theory and experiment.

Assuming a regular donor arrangement, analytic expressions were obtained in Ref. 8 that describe the time evolutions of the population in the case of the hopping mechanism of migrational quenching. These equations permit, in principle, determination of the microparameter C_{DD} in accord with the indicated scheme. They were obtained in Ref. 8, however, assuming a zero minimum distance R_0 between the donor and acceptor, so that an infinite quenching rate was obtained at $t=0$, making it difficult to compare the theory with experiment over the entire time scale.

In the present paper, within the scope of the approach used in Ref. 8, we consider for a dipole-dipole interaction the kinetics of hopping quenching at $R_0\neq 0$, obtain approximate formulas for the quenching kinetics at characteristic values of the parameters of the theory, and demonstrate by numerical calculation the accuracy of the derived formulas. For a primitive cubic lattice we compare the integral approach with that developed in Ref. 7 for the description of the decay kinetics of an excited donor state, with allowance for the actual structure of the crystal.

We express the decay kinetics of an excited state of a donor system following δ excitation in the form

$$I(t)=I(0)\exp\{-t/\tau_D-\Pi(t)\}, \tag{1}$$

where $\Pi(t)$ is the nonradiative-energy-transfer function and τ_D is the donor proper lifetime. The expression obtained in Ref. 8 for $\Pi(t)$, in the case of the dipole-dipole transfer mechanism that will be discussed below, is

$$\Pi(t)=\frac{2}{3}\pi^2 n_A (C_{DA}\tau_0)^{1/2}\left[\frac{1}{2}\Phi\left(\left(\frac{t}{\tau_0}\right)^{1/2}\right)+\frac{t}{\tau_0}\Phi\left(\left(\frac{t}{\tau_0}\right)^{1/2}\right)+\exp\left(-\frac{t}{\tau_0}\right)\left(\frac{t}{\pi\tau_0}\right)^{1/2}\right]. \tag{2}$$

Here n_A (n_D) is the density of the acceptors (donors), $\tau_0=(\frac{8}{27}\pi^3 n_D{}^2 C_{DD})^{-1}$ is the most probable donor–donor transfer time[1,2] and represents the time of one excitation hop in an ordered lattice of donors with a certain average distance between them, and

$$\Phi(x)=\frac{2}{\pi^{1/2}}\int_0^x e^{-z^2}dz$$

is the probability integral.[9]

The instantaneous quenching rate $W(t)$ is then

$$W(t)=\frac{d\Pi(t)}{dt}=n_A\int_0^\infty \frac{C_{DA}}{R^6}n(R,t)\,dV$$

$$=\frac{2}{3}\pi^2 n\left(\frac{C_{DA}}{\tau_0}\right)^{1/2}\left\{\frac{1}{\sqrt{\pi}}\left(\frac{\tau_0}{t}\right)^{1/2}e^{-t/\tau_0}+\Phi\left(\frac{t^{1/2}}{\tau_0^{1/2}}\right)\right\}, \tag{3}$$

where $n(R,t)$ is the instantaneous excitation density at a donor located a distance R from an acceptor.[8]

It is impossible to obtain analytic expressions for $\Pi(t)$ and $W(t)$ for a nonzero minimum donor–acceptor distance. We can, however, analyze their asymptotic behavior and investigate the functions $\Pi(t)$ and $W(t)$ by numerical methods.

The general expression obtained from (3) assuming $R_0\neq 0$ is

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$$W(t)=\frac{4}{3}\pi n_A\left(\frac{C_{DA}}{\tau_0}\right)^{1/2}$$

$$\times\left\{\operatorname{arctg} a+e^{-t/\tau_0}\int_0^a e^{-tx^2/\tau_0}\,dx-e^{-t/\tau_0}\int_0^a\frac{e^{-tx^2/\tau_0}}{1+x^2}\,dx\right\}, \quad (4)$$

$$\Pi(t)=\int_0^t W(t')\,dt',$$

where

$$a=(\tau_0/\tau_1)^{1/2}, \qquad \tau_1=(C_{DA}/R_0^6)^{-1}.$$

At short time ($t\ll\tau_1$) as well as when the kinetic quenching stage[2] is realized ($a\ll 1$), we have from (4) at all values of the time

$$W(t)\approx{}^4/_3\pi n_A C_{DA}/R_0^3. \quad (5)$$

Obviously, in both cases (static and dynamic ordering) the densities of the donor excitations are the same at all donors. This follows automatically from the expression given in Ref. 8 for $n(R,t)$. We note that at $t\ll\tau_1$ Eq. (5) is obtained at any ratio of τ_0 and τ_1. The obvious reason is that the migration does not "knock down" (but, on the contrary, enhances) the initial equiprobable excitation distribution realized when the sample is δ-excited.[7]

In the case $\tau_0=\tau_1$ we get from (4)

$$W(t)=\frac{4}{3}\pi n_A\left(\frac{C_{DA}}{\tau_0}\right)^{1/2}$$

$$\times\left\{\frac{\pi^{1/2}}{2}\left(\frac{\tau_0}{t}\right)^{1/2}e^{-t/\tau_0}\Phi\left(\frac{t^{1/2}}{\tau_0^{1/2}}\right)+\frac{\pi}{4}\left[\Phi\left(\frac{t^{1/2}}{\tau_0^{1/2}}\right)\right]^2\right\}. \quad (6)$$

The agreement of one of the experimental $W(t)$ dependences obtained at different densities n_D with that calculated from (6) is evidence of satisfaction of the relation $\tau_0=\tau_1$, and this can be used in the reduction of the experimental data.

If the condition $a\gg 1$ is satisfied we obtain by expanding (4) in powers of $1/a$, we get at arbitrary time (accurate to the first term of the expansion):

$$W(t)\approx\frac{4}{3}\pi n_A\left(\frac{C_{DA}}{\tau_0}\right)^{1/2}\left\{\operatorname{arctg}\left(\frac{\tau_0}{\tau_1}\right)^{1/2}-\frac{\pi}{2}+\frac{\pi}{2}\Phi\left(\frac{t^{1/2}}{\tau_0^{1/2}}\right)\right.$$

$$+e^{-t/\tau_0}\left(\Phi\left(\frac{t^{1/2}}{\tau_1^{1/2}}\right)\left(\frac{\pi^{1/2}}{2}\left(\frac{\tau_0}{t}\right)^{1/2}+\pi^{1/2}\left(\frac{t}{\tau_0}\right)^{1/2}\right)\right.$$

$$\left.\left.-\pi^{1/2}\left(\frac{t}{\tau_0}\right)^{1/2}+e^{-t/\tau_1}\left(\frac{\tau_1}{\tau_0}\right)^{1/2}\right]\right\}. \quad (7)$$

The expression for $\Pi(t)$ takes in this case the form

$$\Pi(t)=\frac{4}{3}\pi n_A(C_{DA}\tau_0)^{1/2}\left\{\frac{\pi}{2}\left(\frac{1}{2}+\frac{t}{\tau_0}\right)\Phi\left(\frac{t^{1/2}}{\tau_0^{1/2}}\right)\right.$$

$$+\frac{\pi^{1/2}}{2}\left(\frac{t}{\tau_0}\right)^{1/2}e^{-t/\tau_0}\left(2\Phi\left(\frac{t^{1/2}}{\tau_1^{1/2}}\right)-1\right)$$

$$\left.+\left(\frac{\tau_1}{\tau_0}\right)^{1/2}\left(e^{-t/\tau_0-t/\tau_1}-\frac{t}{\tau_0}-1\right)\right\}. \quad (8)$$

Letting $\tau_1\to 0$ in (7) and (8) we obviously obtain Eqs. (3) and (2).

Relations (7) and (8) describe the decay of the excited state of the donor in the entire time interval (provided that $a\gg 1$). We note that whereas the functions $\Pi(t)$ and $W(t)$ are in the general case quite complicated, at $W'(t)=\Pi''(t)$ we have an exact expression valid for all values of the parameters and of the time:

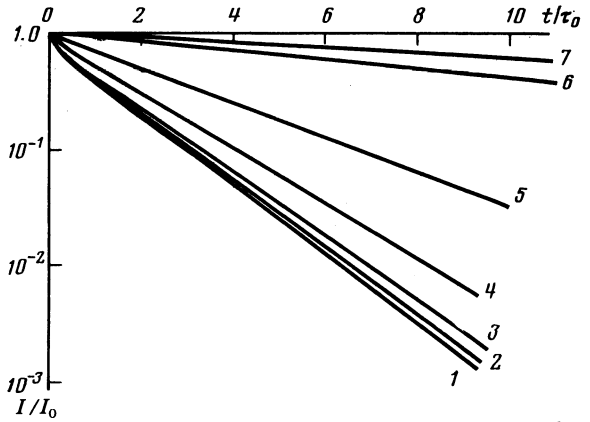

FIG. 1. Temporary evolution of the excited state of the donors, calculated from Eqs. (2)—curve 1; (12)—curves 2, 4, 6; (4)—curves 3, 5, 7, at parameter values $a^2=100$ (curves 2, 3), 1 (curves 4, 5), and 0.01 (curves 6, 7). Curve calculated from approximate Eq. (8) at $a^2=100$ is coincident with curve 3.

$$W'(t)=\frac{4}{3}\pi n_A\left(\frac{C_{DA}}{\tau_1}\right)^{1/2}$$

$$\times\frac{1}{2t}e^{-t/\tau_0}\left\{e^{-t/\tau_1}-\frac{\pi^{1/2}}{2}\left(\frac{\tau_1}{t}\right)^{1/2}\Phi\left(\frac{t^{1/2}}{\tau_1^{1/2}}\right)\right\}. \quad (9)$$

Analyzing with the aid of (9) the $W'(t)$ curves obtained from the experimental data, we can also determine the parameters of interest to us. The figure shows the decay kinetics of the excited state of the donors at fixed values of n_A, n_D, C_{DA}, C_{DD}, calculated from Eqs. (2) (the result of Ref. 8), (4) (the exact integral expression that takes a nonzero R_0 into account), and (8) (an approximate expression valid at $a\gg 1$). The factor $n_A(C_{DA}\tau_0)^{1/2}$, which is common to all the expressions used for $\Pi(t)$ and has the meaning of the relative "black sphere,"[8] was assumed equal to 0.1. The abscissa is the dimensionless time t/τ_0. It can be seen that at the same values of n_A, n_D, C_{DA}, C_{DD} the decay kinetics depends strongly on R_0. It can also be seen that the approximate equations (7) and (8) agree well within the range of their applicability with the exact results. At $a^2\gtrsim 10^4$ the donor-excited-state decay curves plotted from the data of Ref. 8 and from Eqs. (4) and (8) are in almost complete agreement in a population dynamic range that reaches three orders of magnitude. At $t\ll\tau_0$ and $a\gg 1$ we obtain from (4)

$$\Pi(t)\approx\frac{4}{3}\pi n_A(C_{DA}\tau_0)^{1/2}$$

$$\times\left\{\pi^{1/2}\left[\left(\frac{t}{\tau_0}\right)^{1/2}+\frac{1}{3}\left(\frac{t}{\tau_0}\right)^{3/2}\right]\Phi\left(\frac{t^{1/2}}{\tau_1^{1/2}}\right)\right.$$

$$\left.+\left(\frac{\tau_1}{\tau_0}\right)^{1/2}(e^{-t/\tau_1}-1)\right\}. \quad (10)$$

This expression differs from the analogous expression of Ref. 8 (at $t\ll\tau_0$):

$$\Pi(t)\approx\frac{4}{3}\pi^{3/2}n_A C_{DA}^{1/2}\left\{t^{1/2}+\frac{1}{3\tau_0}t^{3/2}\right\}. \quad (11)$$

We note that to analyze the experimental decay curves with the aid of (11) it is necessary to satisfy, besides the condition $t \ll \tau_0$, also $t \gg \tau_1$, whereas the use of (10) does not require satisfaction of the last inequality. Information on C_{DA} is obtained in this case by using the initial section $t \lesssim \tau_1$, where the quenching processes are most strongly pronounced.

It was proposed in Ref. 7 to describe the rate of the hopping quenching by the expression

$$W(t) = \frac{n_A}{N_D} \sum_i W_{DA}(R_i)\, n(R_i, t), \tag{12}$$

$$\Pi(t) = \int_0^t W(t')\, dt',$$

where $n(R_i, t)$ agrees with Ref. 8, W_{DA} is the donor–acceptor interaction probability, and the summation is over the donor-sublattice sites (whose density is N_D). If the donors and acceptors are incorporated in one and the same sublattice, we have (12)

$$W(t) = y_A \sum_i W_{DA}(R_i)\, n(R_i, t), \tag{13}$$

where y_A is the average acceptor density. By describing the experimental donor-excited-state decay curves with the aid of Eqs. (12) and (13), which take the actual crystal structure into account, we obtain good agreement between the theoretical and experimental results.[7]

Let us compare the results of the numerical calculation of the temporal evolutions of the donor-excited-state population, obtained by using the integral approach to the determination of the function $\Pi(t)$ from Eqs. (1) and (4) and with the aid of (12) and (13), for a primitive cubic lattice (see the figure). As expected, the difference between the decay curves is larger the larger the ratio τ_1/τ_0. This circumstance must be borne in mind if the experimental data are reduced with the aid of integral equations that do not take the geometry of the crystal lattice into account.

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Translated by J. G. Adashko